

Investigations of Shock Wave Synthesis of Metastable Compounds

Final Technical Report

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ABSTRACT

In accordance with the contract requirements the investigation of phase formation in $\text{GeO}_2\text{-SiO}_2$ system under the effect of shock waves has been undertaken with the aim of revealing of possibilities of explosion as a preparative method in the chemistry of metastable compounds as well as of investigating of the mechanism of chemical reactions in shock wave. The system has been taken as a model since no compounds were obtained in it by no one traditional method of synthesis and the existence of binary compounds is contradicted on the basis of counter polarization concept in principle. Besides that the realization of chemical processes in the system is made difficult due to high viscosity and low diffusion coefficients of components in solid and melt states. Nevertheless under the effect of shock waves mixed compounds have been synthesized and the scheme of phase formation has been constructed in relation to the intensity of shock wave effect. One of these compounds of wide homogeneity range ($\approx 30\text{-}70$ mol%) is realized in the form of cubic solid solution of fluorite type structure. Besides that the compound of GeSiO_4 composition stabilized by the excess of SiO_2 has been obtained.

It has been found out that the compounds are metastable, and the scheme of phase formation constructed with data of shock wave synthesis is representative of metastable diagram of state realizing in the system $\text{GeO}_2\text{-SiO}_2$ in the conditions of explosion treatment.

Key words: shock wave effect; the system $\text{GeO}_2\text{-SiO}_2$; metastable state.

BACKGROUND OF THE PROBLEM

The advancement of science and techniques depends in many respects upon success in the field of preparation of new materials with specified properties. The possibilities of new materials synthesis by conventional methods of inorganic chemistry are restricted by equilibrium phase diagrams and now are practically exhausted. Large number of the latest achievements in the field of material synthesis relate to the realization of metastable states. Here it should be mentioned metallic glasses, ceramics, high temperature superconductors, superhard materials etc. The development of metastable state physics and chemistry is intimately connected with the elaboration of special production methods permitting to realize metastable states. It is obvious that the larger a nonequilibrium process degree, the larger appearance opportunity of metastable states and materials. Processes governed by the effect of strong shock waves are a limit case of deviation from equilibrium processes. Shock wave effect, characterized by microsecond duration is not a simple superposition of pressure and temperature. Specific features of the effect favorable for metastable state realization are tremendous rates of substance loading (10^{-11} - 10^{-7} time) and subsequent unloading (10^{-7} - 10^{-5} time).

It is known that under the effect of strong shock waves chemical reactions and phase transitions of all types take place [6]. Chemistry of shock waves gained its advancement and developed into some original trend about 30 years ago. To the present rather large quantity of experimental data has been accumulated [7]. However, the mechanism of chemical processes proceeding under the shock wave effect is still unknown, the limits of possibilities of explosion as a production method have not been revealed either.

At present investigations of the mechanism of chemical reactions in shock waves and limits of possibilities of shock-wave synthesis method as a production method in

chemistry of metastable states are necessary condition for shock wave chemistry progress.

The forementioned problems are principal subject of investigations within the limits of the contract. It should be mentioned that the most interesting results in this direction we have obtained in the course of study of the regularities of phase formation in oxide refractory systems of full raw of lanthanides with elements of IV A subgroup [7]; some peculiarities of chemical reaction proceeding under the effect of shock waves have been revealed and some metastable compounds have been synthesized.

So, the present work is natural development of our previous works.

SETTING UP THE PROBLEM

To elucidate the possibilities of shock wave method synthesis in the field of metastable state appearance it was necessary to choos a system in which no compounds have been obtained by no one of recognized methods and in this case the performing of any chemical processes would be hindered at the most in kinetically and thermodynamically. Some such objectives, in particular for oxides of titanium, germanium and stanum is known among silicate systems. Silicate systems are known by their extremely disadvantageous (from the kinetics point of view) processes of chemical interactions governed by a low value of diffusion coefficient in silicon oxide and high viscosity of its melt. Binary systems consisting of GeO_2 and SiO_2 has been selected as the model system with regard to the proximity of physico-chemical properties and the forementioned peculiarities.

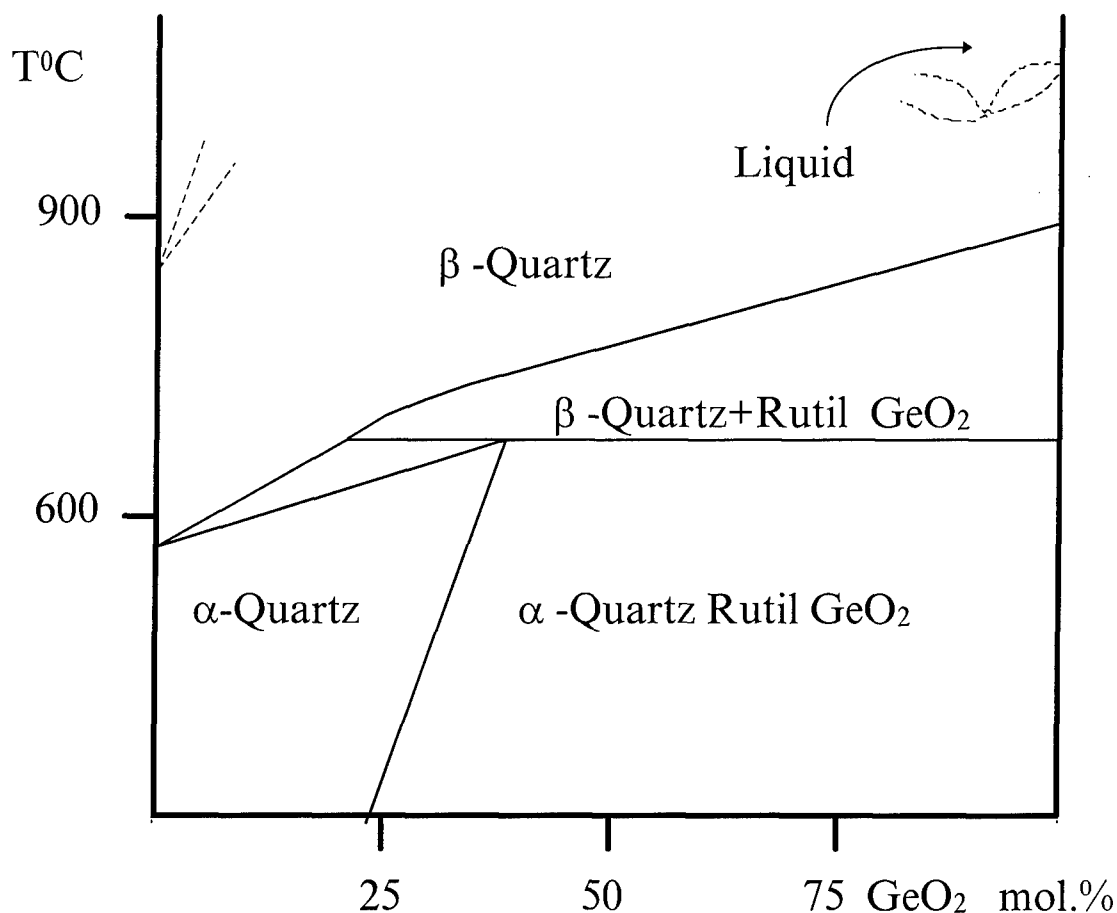


Fig.1 Equilibrium diagram of SiO_2 - GeO_2 system [1].

Available data on GeO_2 - SiO_2 equilibrium diagram of state [1-4] are indicative of no particular compounds (Fig.1); solid solutions of initial components were observed only.

Therefore GeO_2 - SiO_2 system is ideal object of investigations in terms of possibilities of synthesis of mixed compounds in the mixture of initial components.

EXPERIMENTAL

It was necessary to perform some preliminary investigations relative to chemical reactions proceeding in order to arrange experiments for the study of phase-formation in GeO_2 - SiO_2 system. Cylindrical ampoules have been used in the study. Shock wave intensity has been varied by the use of explosives of different power. Cast charges of TNT/RDX 50/50 and 40/60 weight % compositions have been mainly used. Material which ampoules are made from influences the results of shock-wave effect. Ampoules made of steel and copper have been used. Due to larger plastic deformation of reaction zone the parameters of the explosion effect (primarily the temperature) turns out to be larger in the case of copper ampoules in comparison with these of in steel ampoules [6]. The same factor works in the case of use of mixture of different porosity. Particular significance the influence gains in the case of different form of SiO_2 . The influence of three forms of SiO_2 has been studied: α - quartz grinded in a ball mill (particle size 20-80 mkm), quartz glass (particle size 10-100 mkm) and amorphous SiO_2 produced by its precipitation by ammonia from SiCl_4 with subsequent annealing at 400° C. SiO_2 of glass and amorphous forms has been mainly used in the work since it results in the most reproducibility of data, amorphous SiO_2 use relative to glass one being equivalent to the use of more power shock-wave effect.

The values of shock compression pressure evaluated by the technique [8] ranges from 50 to 100 GPa. However, as at present it is not possible to determine the values of pressure and temperature within reactive multicomponent systems it seems that it is more correct to point out concrete conditions of the experiment. The intensity of shock wave effect is conditioned by explosive power, ampoules material and mixture type (glass-like and amorphous SiO_2). With taking these into account the following experimental assembling have been used in order of the increase of shock wave effect intensity: 1 - TNT/RDX 50/50, steel, glass-like SiO_2 ; 2 - TNT/RDX 50/50, copper, glass-like SiO_2 ; 3 - TNT/RDX, steel, amorphous SiO_2 ; 4 - TNT/RDX 50/50, copper, amorphous SiO_2 ; 5 - TNT/RDX 40/60, copper, amorphous SiO_2 .

The mixtures to be investigated were located inside cylindrical ampoules (Lacked density of the samples comprised 50-70% of theoretical one). After an explosion treatment ampoules were open in a lathe and put through a phase analysis by x - ray diffractometer DRON-2.0 ($\text{CuK}\alpha$ - radiation).

RESULTS AND DISCUSSIONS

Investigations performed can be divided into three parts. Preliminary investigations included investigations techniques mastership on the base of some mixtures comprising different type of SiO_2 in relation to explosive power and ampoules material. The data obtained in the course of phase-formation study in GeO_2 - SiO_2 system in a wide concentration range and with different experimental assemblings. The analysis and interpretation of data obtained comprise the third part.

Work under the first stage of the contract comprises the following: production of cylinder recovery devices and explosive charges of different compositions, performance of some scouting experiments to ascertain a crucial possibility of

chemical compounds synthesis under the effect of shock wave loading in GeO_2 - SiO_2 system. Steel and copper recovering devices with axis cavity for specimen of 5-6 mm inner diameter and 50-60 mm length have been used. Gliding detonation wave have been employed for shock-wave loading of mixture under investigation. To accomplish this, cylindrical cast charges of TNT and RDX/TNT of three compositions: 60/40, 50/50, and 40/60 of 1-2 kg weight comprising axis cavities for cylindrical recovery device have been used. In this case the intensity of shock-wave loading increases from TNT to RDX/TNT 40/60 and corresponds to dynamic pressure level of 50-100 GPa.

To produce mixtures for the investigations GeO_2 powder of 99.99% pure and 20-80 mkm particle size and SiO_2 of three modifications: crystalline α - quartz, amorphous quartz produced by its precipitation by ammonia from SiCl_4 with subsequent annealing at 400° C, and quartz glass have been used. Intro-crystallizational water is the main component of SiO_2 modifications impurities, its weight part comprises ~ 2% for α - quartz, 5% for amorphous quartz and smaller than 1% for quartz glass. The density of mixtures inside recovering devices corresponds to 50-70% of their maximum density.

Some scouting experiments with GeO_2 / SiO_2 mixtures of components relation 1 : 1 for α - quartz and amorphous quartz and 2 : 3 for quartz glass (molar relationship) have been performed. After explosion treatment recovered specimen has been withdrawn from the recovering device in a lathe and put through x - ray phase analysis with the use of DRON-2.0 diffractometer ($\text{CuK}\alpha$ - radiation). As the result of the investigations binary compounds have been synthesized on the base of GeO_2 - SiO_2 system. The combined yield of new phases amounts up to 70% in relation to the initial mass of substance under investigation. During the first stage of the work three such compounds have been registered.

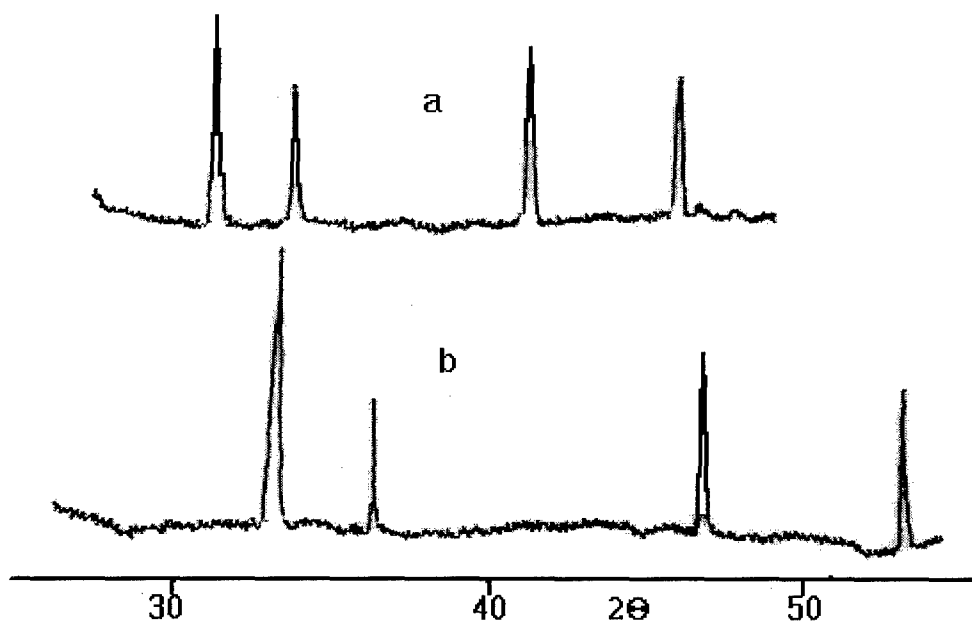


Fig.2 Diffractogram of cubic phase of fluorite type synthesized by explosion in GeO_2 - SiO_2 system:
a) 30 mol.% of SiO_2
b) 60 mol.% of SiO_2

Two compounds of GeO_2SiO_6 and $\text{Ge}_2\text{Si}_3\text{O}_{10}$ approximate composition and of identical structure have been obtained when used the charges of 1 and 2. The third compound appears close to GeSiO_4 composition and originates at the use of shock wave scheme of loading number 3. X - ray analysis of the identical structure compounds has shown that they crystallize into cubic structure of fluorite type with $\text{Fm}\bar{3}\text{m}$ space group. X - ray photographs of the compounds obtained are shown in Fig.2.

The increase of shock wave effect intensity results in the fact that their realization concentration interval widens considerably and closes up near the composition comprising 50 mol % of SiO_2 , the area of homogeneity of cubic solid solution of fluorite type ranging approximately from 30 until 70 mol %. The dependence of unit crystalline cell of cubic solid solution of fluorite type obtained by shock compression is given in Fig.3; the dependence break being found near 50 mol % composition. With increasing of shock wave effect intensity some decrease of solid solution occurrence area and exfoliation of the solution into fluorite-like phases of different compositions near 50 mol % being evident.

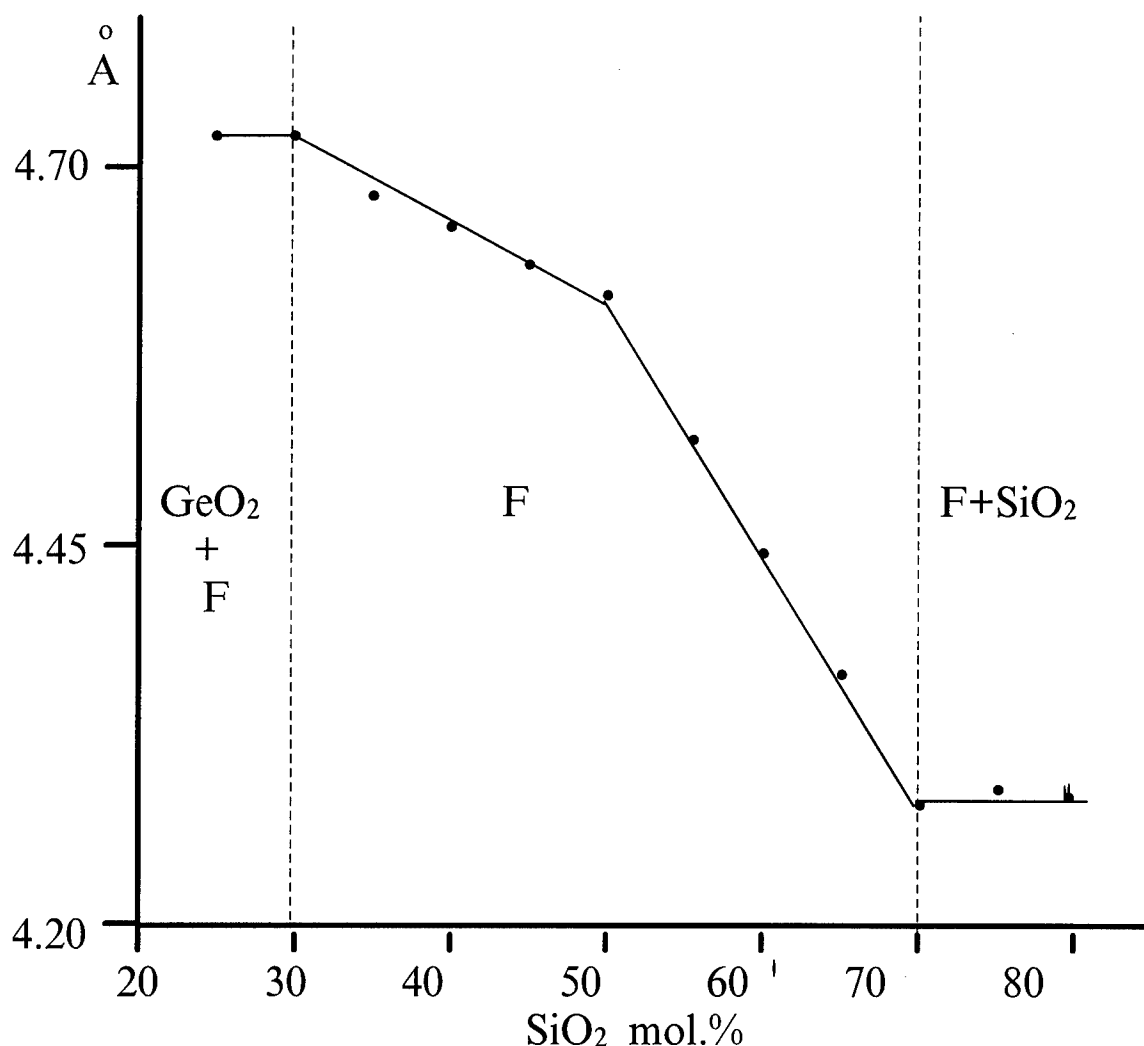


Fig.3 The dependence of a unit crystallographic cell parameter of solid solution of fluorite type on the composition for $\text{GeO}_2 - \text{SiO}_2$ system. F - solid solution of fluorite type

Except for the solid solution it has been possible first to synthesize in GeO_2 - SiO_2 system stoichiometric compound of GeSiO_4 composition performing the synthesis process in steel ampoules and using amorphous SiO_2 in the mixture. X - ray photograph of the compound obtained is shown in Fig.4 and the values of interplane distances are given in Tabl.1. The compound was found to be stabilized by SiO_2 excess and with increasing of shock wave effect intensity (charge assembly 5) decomposes into cubic phases of fluorite type of different compositions.

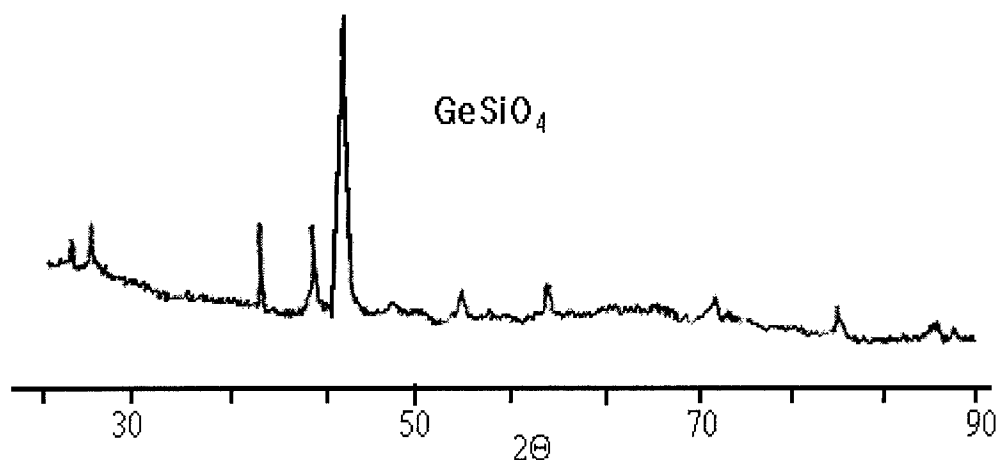


Fig.4 Diffractogram of GeSiO_4 compound obtained under the effect of shock wave.

Table 1.

**Cristallographyc characteristics of GeSiO_4 compound
obtained under the effect of shock wave.**

№	J/J_0	$\frac{0}{A}$	№	J/J_0	$\frac{0}{A}$
1	15	3.420	7	20	1.546
2	20	3.261	8	10	1.318
3	40	2.287	9	8	1.238
4	40	2.101	10	18	1.194
5	100	2.006	11	10	1.116
6	20	1.705	12	6	1.104

Except for the first obtained mixed compounds solid solutions on the base of starting components have been synthesized in the system; up till 5 mol % of SiO_2 is dissolved in GeO_2 and up till 2 mol % of GeO_2 in SiO_2 .

Experimental results of shock wave synthesis in GeO_2 - SiO_2 system have been used to construct the phase-formation scheme in the system in relation to the intensity of shock wave effect (Fig.5).

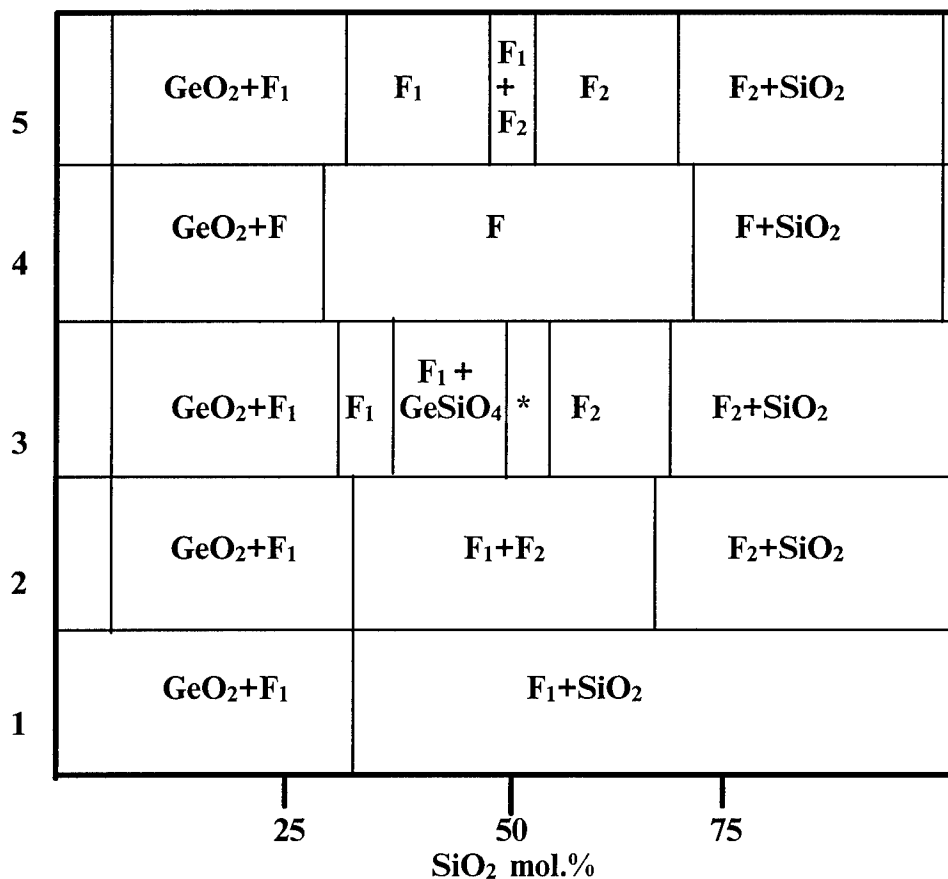


Fig.5 Phase-formation scheme in GeO_2 - SiO_2 system in relation to the intensity of shock-wave effect:

- 1 - TNT/RDX 50/50, steel recovering device, SiO_2 in form of glass;
 - 2 - TNT/RDX 50/50, copper recovering device, SiO_2 in form of glass;
 - 3 - TNT/RDX 50/50, steel recovering device, SiO_2 in form of silica gel;
 - 4 - TNT/RDX 50/50, copper recovering device, SiO_2 in form of silica gel;
 - 5 - TNT/RDX 40/60, copper recovering device, SiO_2 in form of silica gel.
- F** - solid solution of fluorite type
F₁, F₂ - phases of fluorite type of different composition
***** - phase composition $\text{F}_2 + \text{GeSiO}_4$

The scheme shows basic features of diagram of state, in particular main requirements of phases rule are valid. The probable diagram of state of GeO_2 - SiO_2 system has been developed on the base of the data obtained; the diagram is realized in the conditions of shock wave effect (Fig.6). The main feature of the diagram is the presence of the dome

restricting from the underside the cubic solid solution area (Fig.6) which appears as some "bitterfly", inside the dome the compound of GeSiO_4 composition being formed.

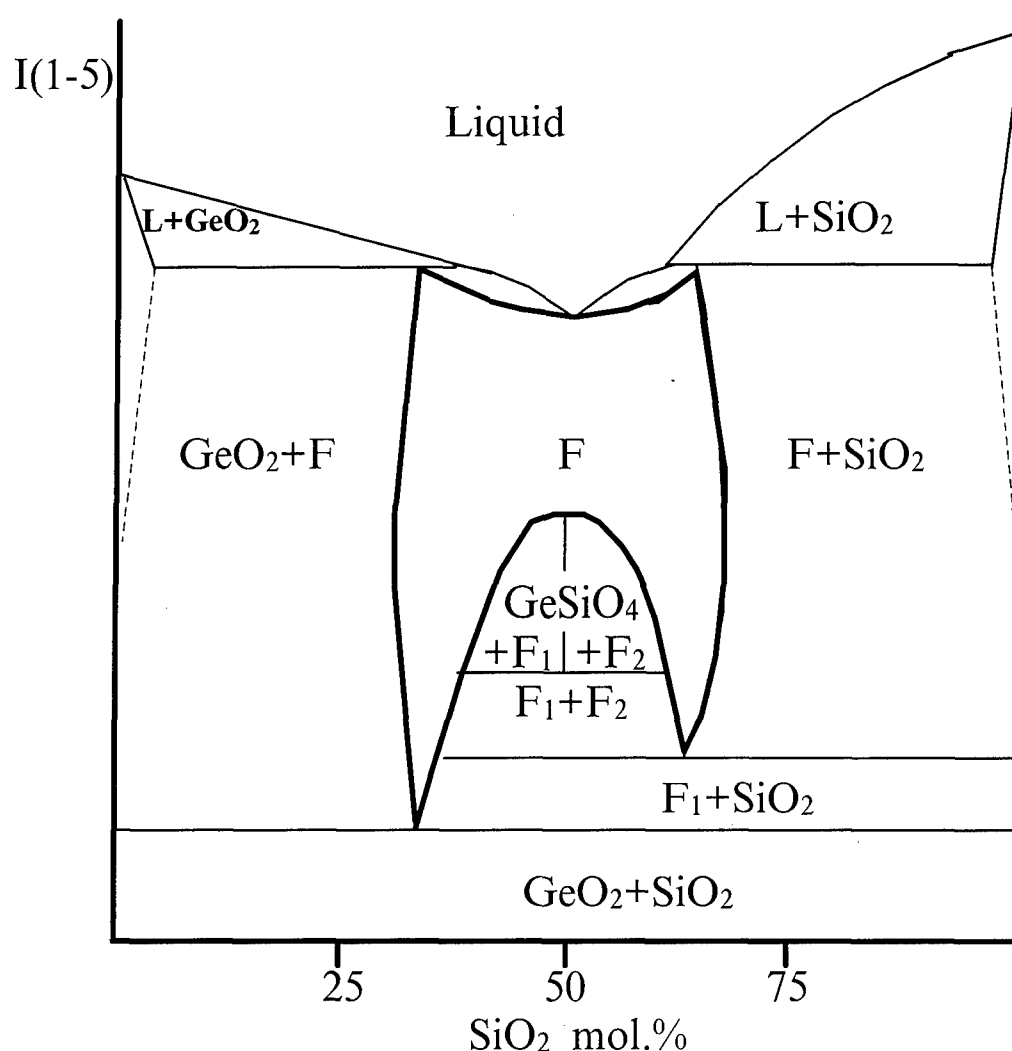


Fig.6 Probable diagram of state of GeO_2 - SiO_2 system realizing at the conditions of shock wave effect.

J(1-5) - intensity of shock wave effect

F - solid solution of fluorite type

F_1, F_2 - phases of fluorite type of different composition

L - liquid

The investigation of thermal stability of the mixed compounds obtained has shown that all the compounds are metastable and begin to decompose at temperatures above 400°C . It follows from the comparison of the diagram with the equilibrium diagram of state (Fig.1) it is possible to hold that it relates to that of metastable one since the phases fields interrelation in the wide concentration range is based on the metastable compounds exactly in the agreement with phases rule and regularly changes with the intensity of the shock wave effect. The fact has engaged attention that the diagram of state constructed (Fig.6) correlates carefully with stable and unstable diagrams of state of titanium systems of rare-earth elements previously investigated [7]; the latter are characterized by the presence of areas of cubic solid solutions of

pyrochlore and fluorite types in the “dome” shape and compounds inside the “dome” (Fig.7).

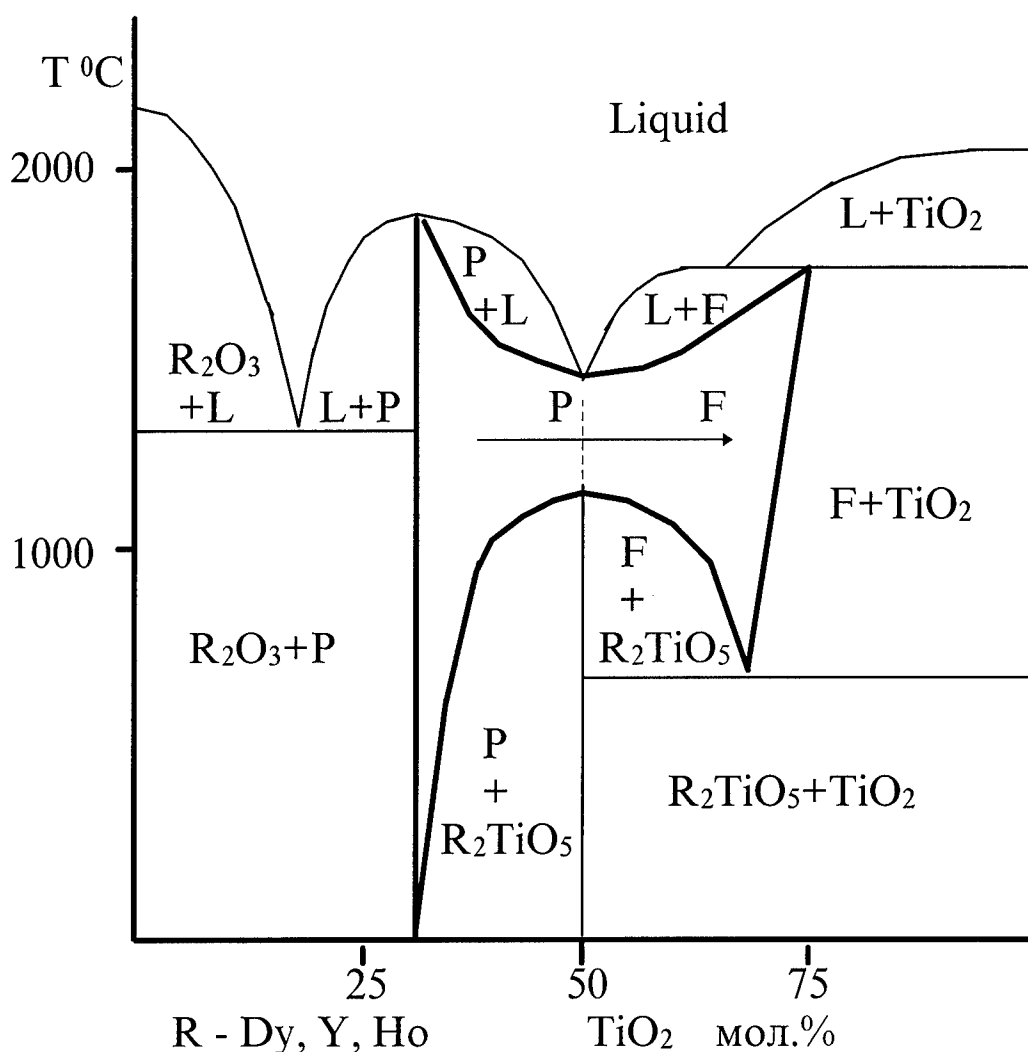


Fig.7 Diagram of state of R_2O_3 - TiO_2 (R -Dy, Y, Ho) systems.
 R_2O_3 - oxides of rare-earth elements
 P - solid solution of pyrochlore type
 F - solid solution of fluorite type
 R_2TiO_5 - orthotitanate
 L - liquid

The zone of crystallization constitutes of transparent crystals of yellowish tint, steps of growth and twins being observed. The data testify that the crystallization proceeds from the melt. The fact engages attention that all conceivable samples reacted completely bear evidence of melting and crystallization. No processes of chemical interaction have been observed where the melt is unavailable. It is interesting to note some characteristic features of the results obtained. It turned out that the new chemical compounds origin takes place only with the use of the most power explosive charges of TNT/RDX 50/50 and TNT/RDX 40/60. In addition, the new phases yield depends on SiO_2 modification used. The best interaction is observed with amorphous SiO_2 . For the same explosive assembly type the yield of the new

compounds and composition of samples reacted depend also on the ampoules material. X - ray studies of the composition of recovered products located along the axis of ampoules and in radial direction have shown that the interaction proceeds nonuniformly over the sample volume. The boundary demarcating region with and without interactions appears as a cone with its base at the cavity bottom and its top of some distance from the cavity beginning (as reviewed from the entrance of shock wave). The most intensive interaction takes place at the cavity bottom in the region of reflected wave action. Glass corresponding to mixtures of different compositions originates frequently at the top part of ampoules, and the region of well crystallized product appears at the lower part.

The fact that sufficiently large crystals of metastable compounds originate under the shock wave effect from the melt testifies that their formation have been going on under conditions of a high overcooling of the melt.

Hence one can hold that the mechanism of chemical reaction in GeO_2 - SiO_2 system under the shock wave effect is governed by the components interaction through the step of melt occurrence, and the state of final products depends on the conditions (primarily on the value of temperature) of crystallization (or solidification in the case of glass origin) of the melt at a high overcooling of the latter.

PRINCIPAL RESULTS AND CONCLUSIONS

Explosion use has made it possible to synthesize first two metastable compounds in GeO_2 - SiO_2 system in which no binary compounds were obtained by none of the known ways and the proceeding of any chemical processes is extremely hampered by kinetic and thermodynamic restrictions. One of compound the is the solid solution having a wide range of homogeneity ($\sim 30 \div 70$ mol %) crystallizes in cubic structure of fluorite type, the second - is stoichiometric compound of GeSiO_4 composition stabilized by excess SiO_2 . It has been shown that all the compounds are metastable and is separated on heating even at temperature higher than 400°C .

The scheme of phase-formation in GeO_2 - SiO_2 system has been constructed from the data of shock wave synthesis. It has been shown that the scheme is some image of the system metastable diagram of state.

Relaying on the study of the recovered products of shock wave synthesis in GeO_2 - SiO_2 system the mechanism of phase-formation under conditions of the shock wave effect on substance has been proposed. According to the mechanism the occurrence of melt is the necessary condition for the components' interaction, and the final product composition is governed by a high overcooling of the melt down till some proper temperature where by the processes of crystallization and glass formation proceed.

So, based on the experimental data obtained for GeO_2 - SiO_2 system as an example, one can hold that explosion use as a production method allows to extend substantially the capabilities of new compounds and materials synthesis on metastable states realization under the shock wave effect even in systems having the most unfavorable (from kinetic and thermodynamic point of view) properties hampering the occurrence in the systems of any chemical processes.

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